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(54) **Radical polymerization process**

(57) A polymerization process comprising: heating a mixture comprised of a free radical initiator, a stable free radical agent, at least one polymerizable monomer compound, and optionally a solvent, to form a polymer with a high monomer to polymer conversion and a nar-

row polydispersity, wherein said polymer is comprised of a covalently bound free radical initiator fragment at one end and a covalently bound stable free radical compound at the other end of the polymer, and wherein said stable free radical agent has high thermal, acidic, and photochemical stability.

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Description

The present invention is generally directed to processes for the preparation of homopolymers and copolymers.

Many polymerization processes used for the synthesis of narrow polydispersity resins, such as anionic, cationic, and group transfer polymerization processes, are severely limited by the need for anhydrous reaction conditions and monomers which do not contain protic or reactive functional groups, for example, hydroxy (OH) carboxy (CO₂H), amino (NH), and the like. As a consequence, these processes are not readily applicable to the polymerization of functionalized monomers since these monomer materials tend to be hydroscopic and any associated water may readily destroy the polymerization initiator component, for example, the hydrolysis or protonation of organolithium reagents by the monomer in anionic polymerization processes, or in other ways cause the polymerization to fail entirely or to be industrially inefficient.

It is generally accepted that known anionic and cationic polymerization processes used for the preparation of narrow polydispersity resins, block and multiblock polymers are not believed possible in aqueous or protic solvent containing polymerization media, or the aforementioned protonic or reactive functional groups, reference the aforementioned US-A-5,312,704.

Of the known polymerization processes a preferred way to prepare polymers or copolymers having a narrow molecular weight distribution or polydispersity is by anionic processes. The use and availability of resins having narrow polydispersities in industrial applications is limited because anionic polymerization processes must be performed in the absence of atmospheric oxygen and moisture, require difficult to handle and hazardous initiator reagents, and consequently such polymerization processes are generally limited to small batch reactors. In addition, the monomers and solvents that are used must be of high purity and anhydrous thereby rendering the anionic process more expensive than alternatives which do not have these requirements. Thus, anionic polymerization processes are difficult and costly. It is desirable to have free radical polymerization process that provides narrow molecular weight distribution homoacrylate containing resins that overcomes the shortcomings and disadvantages of the aforementioned anionic polymerization processes.

Similarly, group transfer polymerization (GTP) processes have limitations and disadvantages, such as anhydrous reaction conditions and expensive reagents, which disadvantage GTP processes particularly for large scale industrial applications.

Free radical polymerization processes are generally chemically less sensitive than anionic processes to impurities in the monomers or solvents typically used and are substantially or completely insensitive to water. There has been a long felt need for an economical free radical polymerization process which is suitable for preparing narrow polydispersity resins in the presence of water.

Conventional free radical polymerization processes that are used to polymerize monomers in general, and functionalized monomers in particular inherently give broad polydispersity resin products or require that sophisticated processing conditions and materials handling protocols be employed.

Copolymers prepared by conventional free radical polymerization processes inherently have broad molecular weight distributions or polydispersities, generally greater than about four. One reason is that most free radical initiators selected have half lives that are relatively long, from several minutes to many hours, and thus the polymeric chains are not all initiated at the same time and which initiators provide growing chains of various lengths at any time during the polymerization process. Another reason is that the propagating chains in a free radical process can react with each other in processes known as coupling and disproportionation, both of which are chain terminating and polydispersity broadening reaction processes. In doing so, chains of varying lengths are terminated at different times during the reaction process which results in resins comprised of polymeric chains which vary widely in length from very small to very large and thus have broad polydispersities. If a free radical polymerization process is to be enabled for producing narrow molecular weight distributions, then all polymer chains must be initiated at about the same time and premature termination by coupling or disproportionation processes must be avoided or eliminated.

One known method of achieving control of polymer molecular weight is through the use of efficient chain transfer agents, but this approach has several drawbacks. This approach irreversibly incorporates the structure of the chain transfer agent into the polymer chain. This can be undesirable since that structure will have an increasing effect on the properties of the polymer as molecular weight decreases. Furthermore, the chain transfer agents commonly employed are mercaptans. These materials are expensive and have objectionable odors associated with their presence. Other common chain transfer agents are hypophosphites, bisulfites, halogenated hydrocarbons such as carbon tetrabromide, and alcohols. These also add to the cost of the process, introduce undesired functionality or properties to the polymer, can introduce salts into the product, and may necessitate an additional product separation step to remove the chain transfer agent from the reaction mixture.

Another way of lowering the molecular weight of the polymer product is by increasing the amount of free radical initiator. This approach adds considerably to the cost of production and may result in polymer chain degradation, crosslinking, and high levels of unreacted initiator remaining in the product. In addition, high levels of initiator may also

result in high levels of salt by-products in the polymer mixture which is known to be detrimental to polymer performance in many applications. The same is true for chain stopping agents such as sodium metabisulfite.

High levels of metal ions together with high levels of free radical initiator have also been tried as means for controlling molecular weight. This method is taught in US-A-4,314,044 where the ratio of initiator to metal ion is from about 10:1 to about 150:1 and the initiator is present from about 0.5 to about 35 percent based on the total weight of the monomers. Such an approach is unsuitable for some products, such as water treatment polymers, which can not tolerate metal ion contaminants in the polymer product. In addition, the product is usually discolored due to the presence of the metal ions. Thus, polymerization processes which produce product polymers containing residual non-polymeric materials may be significantly negatively compromised with respect to, for example, appearance, performance and toxicity properties. Polymeric processes which create or contain non-polymeric residual materials are preferably avoided.

In polymerization reaction processes of the prior art, various significant problems exist, for example difficulties in predicting or controlling both the polydispersity and modality of the polymers produced. These polymerization processes produce polymers with high weight average molecular weights (M_w) and low number average molecular weights (M_n) resulting in broad polydispersities or broad molecular weight distribution (M_w/M_n) and in some instances low conversion. Further, polymerization processes of the prior art, in particular free radical processes, are prone to generating excessive quantities of heat since the polymerization reaction is exothermic. As the viscosity of the reaction medium increases dissipation of heat becomes more difficult. This is referred to as the Trommsdorff effect as discussed and illustrated in *Principles of Polymerization*, G. Odian, 2nd Ed., Wiley-Interscience, N.Y., 1981, page 272, the disclosure of which is entirely incorporated herein by reference. This is particularly the situation for reactions with high concentrations of soluble monomer, for example greater than 30 to 50 percent by weight soluble monomer, which are conducted in large scale reactors with limited surface area and limited heat dissipation capacity. Moreover, the exothermic nature of free radical polymerization processes is often a limitation that severely restricts the concentration of reactants or the reactor size upon scale up.

Further, gel body formation in conventional free radical polymerization processes may result in a broad molecular weight distributions and/or difficulties encountered during filtering, drying and manipulating the product resin, particularly for highly concentrated reactions.

Thus, there remains a need for polymerization processes for the preparation of narrow polydispersity polymeric resins by economical and scalable free radical polymerization techniques and which polymers retain many or all of their desirable physical properties, for example, hardness, low gel content, processibility, clarity, high gloss durability, and the like, while avoiding the problems of gel formation, exotherms, volume limited and multi-stage reaction systems, complex purification, encumbered or comprised performance properties due to undesired residuals or broad polydispersity properties of the polymer resin products, and the like, associated with prior art free radical polymerization methodologies.

There also remains a need for improved stable free radical moderated polymerization processes wherein specifically selected stable free radical agent compounds are employed for controlling polymerization processes, for imparting greater stability to the polymer products and to the reaction process, and which improved stable free radical agent compounds and polymerization processes overcome the aforementioned limitations and problems.

The polymerization processes and the resultant thermoplastic resin and elastomer products of the present invention are useful in many applications, for example, as a variety of specialty applications including toner and liquid immersion development ink resins or ink additives used for electrophotographic imaging processes, or where monomodal or mixtures of monomodal narrow molecular weight resins or block copolymers with narrow molecular weight distribution within each block component are suitable, for example, in thermoplastic films, electrophotographic marking materials such as toners and toner additives, and aqueous or organic solvent borne coating technologies.

One object of the present invention is to provide improved stable free radical agent moderated polymerization processes or pseudoliving polymerization processes and polymers therefrom that overcome many of the problems and disadvantages of the aforementioned prior art.

Another object of the present invention is to provide improved stable free radical moderated polymerization processes for the preparation of thermoplastic resins and elastomers.

In one embodiment of the present invention there is provided a polymerization process for the preparation of thermoplastic resins or elastomers comprising heating a mixture comprised of a free radical initiator, a stable free radical agent, at least one polymerizable monomer compound, and optionally a solvent, to form the thermoplastic resin or elastomer polymer product with a high monomer to polymer conversion and a narrow polydispersity, wherein said product is comprised of a covalently bound free radical initiator fragment at one end and a covalently bound stable free radical compound at the other end of the product, and wherein said stable free radical agent has improved thermal, acidic, and photochemical stability as a discrete molecular entity and as an end group bound to the polymer product.

In one embodiment there is provided thermoplastic and elastomer polymerization processes for the production of diblock and multiblock polymers with high monomer to polymer conversion and narrow polydispersity properties.

In another embodiment of the present invention there is provided thermoplastic resin and elastomer polymerization processes which do not require the use of water or organic solvents, or chain transfer agents as a means of controlling the molecular weight of the resulting polymers.

One embodiment provides polymerization processes which result in narrow polydispersity thermoplastic and elastomer resin products having number average molecular weights above about 1,000.

Another embodiment provides thermoplastic resin and elastomer mixtures having number average molecular weights above about 1,000 to about 200,000 and a polydispersity within the range of from about 1.0 to about 2.0 and which polydispersities are easily selectable and controllable by an operator.

Another embodiment provides a polymer or polymer mixtures having sufficiently low polydispersity properties and high monomer conversions such that residual monomer levels are low and are within industrially acceptable levels so as to avoid additional monomer removal or recovery steps.

Another embodiment provides a polymerization reaction system which affords narrow polydispersity homopolymeric or copolymeric thermoplastic resin products in high yield.

Another embodiment provides a polymerization reaction system which may be conducted in the presence of a minimum amount of conventional reaction media such as water and mixtures of water and water miscible organic solvents.

In yet another embodiment, coupling or disproportionation termination reactions are substantially minimized or eliminated by reversibly terminating the propagating free radical chains with selected stable free radical agent compounds having preferred stability properties, for example, a sterically hindered phenoxy or phenoxide derived stable free radical agent, which both enables and serves to moderate the exothermicity and modality properties of the polymerization processes.

In another embodiment is provided the acceleration of the dissociation of free radical peroxide initiator compounds by the addition of dissociation promoter compounds which include, for example, tertiary amines, which compounds ensure that all polymeric chains are initiated nearly simultaneously or at about the same time very early on in the polymerization process.

In another embodiment is the addition of small amounts of organic or inorganic acids, for example, organic sulfonic and carboxylic acids, to the reaction medium to alter the normal rate of unsaturated monomer reaction without significantly broadening the polydispersity of the polymeric resins and without inducing autopolymerization effects.

Still another embodiment is to prepare water soluble thermoplastic resins or elastomers by single pot processes employing suitable monomer or monomers, free radical initiator, optional minimal amounts of an emulsifier or surfactant which may provide rate enhancement or simplify isolation, but avoids emulsification or phase separation during the polymerization, and certain sterically hindered and highly stabilized stable free radical agent compounds having particularly high thermal, acidic, and photochemical stability, and which stabilized stable free radical compounds form thermally labile bonds with propagating polymeric free radical species wherein the aforementioned thermally labile bond is labile at temperatures above of from about 100 to 250°C.

Another embodiment is to prepare thermoplastic resins and elastomers using polymerization processes wherein the molecular weight of the growing polymer or copolymer chains increase over the entire time period of the polymerization reaction and wherein the percent conversion or degree of polymerization of monomer to polymer with respect to time or number average molecular weight is approximately linear, that is, polymerization processes which occur without the aforementioned Trommsdorff effect.

Moreover, another embodiment is to provide polymerization processes for the preparation of thermoplastic resins and elastomers with narrow polydispersity properties and which polymerization processes are accomplished in a time efficient and economic manner by the optional addition of dialkyl sulfoxides promoter compounds, such as dimethyl sulfoxide (DMSO), and which promoter compounds enable a greater narrowing of the polymer product polydispersity during product formation. The dialkyl sulfoxide additives are preferably liquid at the polymerization reaction temperature and may be used in amounts from about several tenths of a weight percent of the total reaction mixture, to use in amounts as the exclusive reaction solvent or reaction media, for example, in excess of 95 percent by weight of the monomer being polymerized.

In another embodiment of the present invention is provided stable free radical polymerization processes wherein improved levels of free radical initiator efficiency and efficacy are realized and result from the reaction of, for example, benzoyl radicals with a stable free radical precursor compound such as a hindered phenol to produce a stable free radical agent phenoxy radical in situ without the need for preparing the stable free radical compound in a separate or additional step.

In yet another embodiment of the present invention is provided, in embodiments, a thermoplastic polymer resin or elastomer of the formula I - $(M)_n$ - SFR wherein I is a covalently bonded free radical initiator fragment, $(M)_n$ is at least one contiguous polymeric segment comprised of at least one free radical polymerized monomer compound M, n is an integer from about 10 to about 20,000 and represents the total number monomer units contained in the polymeric segment, and SFR is a covalently bonded stable free radical agent, wherein the stable free radical agent possesses

high thermal stability, high acid stability, high photochemical stability, and low toxicity.

In still yet another embodiment is provided, in embodiments, a thermoplastic polymer resin or elastomer containing a covalently bound stable free radical terminal group which possesses high reactivity and high dissociability with propagating free radical polymeric species and is comprised of a sterically hindered stable free radical bearing atom, such as highly substituted organic hydrazyls, organic verdazyls, pyridinyl compounds, organic aroxyis, aryl alkyls and aryl cycloalkyls in which the unpaired electron is on a carbon atom in the alkyl or cycloalkyl group, and mixtures thereof.

In one embodiment the present invention relates to improved polymerization processes which provide homopolymer and copolymer resin products which possess narrow polydispersity properties and which polymerization processes proceed with high monomer to polymer conversion. In particular, this invention relates to improved stable free radical mediated or pseudoliving polymerization processes which yield homopolymers and copolymers having number average molecular weights (M_n) above about 100 to about 1,000 and having a polydispersity ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n) of from about 1.0 to about 2.0 and which processes accomplished in accordance with the present invention provide numerous operational and economic advantages associated therewith.

The present invention provides in embodiments a pseudoliving polymerization process that enables the synthesis of narrow polydispersity homopolymer and copolymer resins from a variety of free radical reactive monomers. The process can, in embodiments, use known free radical initiators in combination with specific non-nitroxide type stable free radical agent compounds and free radical reactive monomers to afford narrow polydispersity thermoplastic resins or elastomers.

The free radical initiator compounds selected must satisfy certain maximum half-life requirements for the purpose of providing efficient and highly controlled polymer chain initiation. The stable free radical agent compounds selected must satisfy certain stability requirements including high thermal stability, and high resistance to degradation by acids or photochemical means. The non-nitroxyl type stable free radical compounds must not initiate nor excessively inhibit or retard desired polymerization processes. The stable free radical agent compounds selected must also satisfy certain bond energy and steric hindrance requirements when the stable free radical agent compound is attached to the end of the propagating polymer chain.

In other embodiments the polymerization processes of the present invention can be used to prepare block copolymers and multi-block polymer having narrow polydispersity properties wherein at least one of the blocks is optionally water soluble thereby providing, for example, a means for preparing surface active or surfactant materials having well defined polydispersity and hydrophobe-lipophile balance (HLB) properties.

The present invention, in embodiments, enables the preparation of homopolymers, random copolymers, block and multiblock copolymers, and polymer blends, with operator selectable molecular weight and polydispersity properties, and which preparation was heretofore not achievable in stable free radical moderated, free radical initiated polymerization systems.

The present invention will be described further, by way of examples, with reference to the accompanying drawings, in which:-

Figures 1,2 and 3 illustrate exemplary substituted and sterically hindered: phenoxy radical compound, tocopherol radical compound, and N-trinitrophenyl-N',N'-diphenyl hydrazine derivative radical, respectively, which compounds are useful as a stable free radical agent in the present invention.

The present invention provides improved stable free radical mediated polymerization processes for preparing polymers, such as thermoplastic resins or elastomeric materials with well defined molecular weight properties and narrow polydispersities. The processes can be run as batch, semi-continuous or continuous processes. The processes provide for from about 1 to about 99 percent by weight of the reaction mixture to be a free radical reactive monomer or monomer mixtures and the processes are conducted at from about 100°C to about 250°C. The processes produce polymer products which have operator selectable low, intermediate, or high molecular weight; narrow polydispersity; low residual salt content or are salt free; possess greater thermal and acidic stability; and low toxicity.

In embodiments, the present invention overcomes many of the problems and disadvantages of related free radical or other polymerization processes by forming narrow polydispersity polymeric resins and wherein high conversion from monomer to polymer is achieved, for example, a polymerization process comprising heating a mixture comprised of a free radical initiator, a non-nitroxyl type stable free radical agent, at least one polymerizable monomer compound, and optionally a solvent, to form the thermoplastic resin or elastomer polymer product with a high monomer to polymer conversion and a narrow polydispersity, wherein said product is comprised of a covalently bound free radical initiator fragment at one end and a covalently bound stable free radical compound at the other end of the product, and wherein said stable free radical agent has high thermal, acidic, and photochemical stability. The stable free radical compound when covalently bound to the polymer chain or product preferably has no unpaired electrons, that is, has no free radical character or free unpaired electrons.

"High thermal stability" refers to stable free radical compounds that do not undergo any apparent or substantial non-productive type thermal degradation, dissociation, or decomposition during the course of the polymerization re-

action processes and subsequent optional isolation steps.

"High acid or acidic stability" refers to a stable free radical compound that does not undergo, to any significant extent, that is to any level which would depart from the objects of the present invention, any apparent or substantial acidic, acid catalyzed, or acid mediated degradation, dissociation, or decomposition to form a non free radical compound with the exception of being covalently bonded to the terminus of the polymeric chain, during the course of the polymerization process and subsequent optional isolation steps.

"High photochemical stability" as used herein is intended to indicate that the stable free radical compounds selected, in embodiments, of the present invention do not undergo to any significant extent, that is to a level which would depart from the objects of the present invention, any apparent or substantial photochemical, photon induced or catalyzed, photolysis, degradation, dissociation, or decomposition to form a non stable free radical compound with the exception of reversible bonding to or debonding from the terminus of the polymeric chain, and which reversible photochemical processes may occur during the course of the polymerization process or subsequent optional isolation steps.

Suitable non-nitroxyl type stable free radical compounds for use in the present are known, and can be prepared prior to mixing with the other polymerization reactants or they may be generated in situ or on an as needed basis, reference for example, the non-nitroxyl type stable free radical compounds described in "Free Radicals" Volumes I and II, edited by J.K. Kochi, Wiley-Interscience, New York, 1973.

The stable free radical agent compounds of the present invention may be generated in any suitable fashion from the corresponding non-free radical precursor, for example, thermally, chemically, electrochemically, photolytically, mechanically, and the like methods.

Examples of suitable and preferred stable non-nitroxyl type free radicals are disclosed in the aforementioned U. S. Patent No. 3,600,169 to Lawton and include: nitrogen centered stable free radical such as organic hydrazyls, verdazyls, and pyridinyl compounds; non-nitroxide oxygen centered stable free radicals such as aroxyls and the like; and carbon centered stable free radicals such as aryl alkyls and aryl cycloalkyls with the unpaired electron residing on a carbon atom in the alkyl or cycloalkyl substituents.

The preferred stable free radical compounds selected for use in the present invention are chosen so as to enhance stability properties of the overall process and products therefrom by providing: stable free radical agent compounds with greater thermal, acidic, and photochemical stability; and polymeric products containing the aforementioned preferred or "stabilized" stable free radical compounds and which "stabilized" compounds, in turn impart greater thermal, acidic, and photochemical stability upon the polymeric products.

The term "stabilized" as used in the context of a stabilized stable free radical agent or compound of the present invention is intended to indicate that a bimolecular reaction of the stable free radical compound (SFR•) with another stable free radical compound (SFR•) of the same or similar type or identity, also known as bimolecular "self" reactions, to form a dimeric product (SFR-SFR) does not occur to any significant extent in the presence of free radical initiator (I•) species, free radical reactive monomers (M), or propagating polymeric chain free radical species (P•) "Stable" does not mean that the stable free radical compound (SFR•) will not react with any other molecule or other free radical, such as a propagating polymeric chain free radical (P•). On the contrary, the stable free radical compounds selected for use in the present invention must readily react, that is, with a rate that is faster than the rate of chain propagation and preferably at or near diffusion control, with the incipient or propagating free radical oligomeric or polymeric chains (P•) to be effective. The reverse reaction under the polymerization reaction conditions is believed to be equally rapid.

C-O• based stable free radicals

Sterically hindered phenoxy stable free radical species useful in the present invention can be conveniently generated in a heterogeneous manner by, for example, contacting a solution of the corresponding phenol with insoluble silver oxide or lead dioxide salts. Alternatively, the phenoxy radicals can be generated by mixing solutions of the corresponding phenol (Ar-OH) or hydroperoxide (Ar-O-OH) and cerium salt solutions, such as ceric ammonium sulfate or nitrate. The phenoxy radicals are preferably prepared and used in the polymerization processes without by-product salts or unreacted phenol being present in substantial amounts.

In preferred embodiments, the sterically hindered phenoxy stable free radical compounds and related stable free radical compounds of the present invention, reference the Figures and the relevant disclosure of stable free radical compounds, also have bulky blocking substituents at one or both of the meta positions and preferably at the para position. Preferred bulky alkyl substituents are, for example, adamantyl (Ad-), sec-butyl (s-Bu-), substituted phenyl (R_n-Ph-), and the like groups. A particularly preferred bulky substituent is tertiary butyl (Me₃C- or t-Bu-) and is preferred because of the effectiveness of this substituent in preventing undesirable and counterproductive side reactions to the phenol aromatic nucleus, and the relative commercial availability and the relatively low cost of the material. Thus, a preferred phenoxy radical for use in the polymerization processes of the present invention is derived from the corresponding phenol of, for example, 2,6-di-tert-butyl-4-methylphenol, and a more preferred phenoxy radical is likewise

derived from 2,4,6-tri-tert-butylphenol. Another preferred compound is 2,6-di-tert-butyl- α -(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-toloxo free radical which is the known galvinoxyl stable free radical.

C• based stable free radicals

Other preferred stable free radicals are those based on hindered substituted triphenyl methane compounds, and the like compounds, and more preferably those substituted by electron-donating substituents, as for example, methoxy groups, and more preferably where such substituents are at the ortho or para position to the radical bearing substituent or site.

N• based stable free radicals

Other preferred stable free radicals are those based on hindered substituted triphenyl amines, and more preferably those substituted by electron-donating substituents, as for example, methoxy groups, and more preferably where such substituents are at the ortho or para position to the radical bearing substituent or site.

Other preferred stable free radicals are those based on the hindered substituted diphenylpicrylhydrazine, and more preferably those substituted by electron-donating substituents, as for example, methoxy groups. Other preferred stable free radicals are those based on the hindered substituted iminoxy radicals, $R_1R_2C=N-O\bullet$, and more preferably those where the R substituents are electron-donating substituents, as for example, methoxy groups, and even more preferably where the R substituents are substituted phenyl groups.

In embodiments, the present invention provides free radical reactive monomer polymerization processes for the preparation of thermoplastic resins or elastomer materials comprising heating from about 100 to about 250°C for a time period of about 30 minutes to about 20 hours a mixture comprised of a free radical initiator (I - I), a stable free radical agent (SFR•) or equivalent precursor compound (SFR-H), at least one polymerizable monomer compound (M), and optionally a solvent, to form a product of the formula $I-(M)_n-SFR$ comprised of a covalently bound free radical initiator fragment (I•) at one end, a covalently bound stable free radical compound (SFR•) at the other end of the product, and with polymerized monomers $(M)_n$ disposed therebetween, where n is an integer from about 10 to about 20,000 and represents the number of monomers in the polymer, and wherein said stable free radical agent has high thermal, acidic, and photochemical stability; optionally cooling the reaction mixture; and optionally isolating, washing, and drying the resulting polymeric product, wherein the product possesses a narrow polydispersity of from about 1.0 to about 2.0, and preferably from about 1.0 to about 1.5, a modality of 1, and wherein a monomer to polymer conversion of from about 10 to about 100 percent is achieved.

The foregoing process can, in embodiments, be expanded to enable the formation of bimodal, multimodal, and the like thermoplastic resins or elastomers, reference for example, US-A-5,322,912. In a specific illustrative example, reaction by heating a mixture of n-butyl acrylate, benzoyl peroxide free radical initiator, and 2,4,6-tri-tert-butylphenoxy stable free radical agent affords a first product resin of poly(n-butylacrylate); further addition of a second monomer such as styrene, additional free radical initiator, and additional phenoxy derived stable free radical compound followed by, or concurrent with, heating provides the product resin mixture of poly(n-butyl acrylate-b-styrene) and homopolystyrene, wherein the homopolystyrene product is of comparable molecular weight to the styrene block segment incorporated into the accompanying poly(butyl acrylate-b-styrene) block copolymer. The product resins each have a covalently bonded benzoyl fragment at one end arising from the free radical initiator and a covalently bonded phenoxy group arising from the stable free radical agent at the other end of the polymer molecules.

In other embodiments of the present invention, there are provided polymerization processes for the preparation of diblock thermoplastic resin comprising: adding to aforementioned first formed thermoplastic resin, either in situ or in a separate reaction vessel, a second mixture containing only monomer comprised of at least one polymerizable monomer compound, wherein the polymerizable monomer compound of the second mixture contains different monomer components from the polymerizable monomer compound of the first polymerized mixture, and wherein there is formed a combined mixture; heating the combined mixture to form a third mixture comprised of a diblock copolymer product comprised of a first product resin formed from the first thermoplastic resin and the second monomer; cooling the third mixture; optionally isolating the diblock copolymer thermoplastic resin product from the third mixture and wherein the diblock copolymer thermoplastic resin possesses a narrow polydispersity.

In still other embodiments of the present invention, there are provided homopolymer and copolymer polymerization processes for the preparation of monomodal multiblock copolymer thermoplastic resin comprising: heating a first mixture comprised of a free radical initiator, a suitable stable free radical agent, and at least one polymerizable monomer compound to form a first intermediate product resin; adding to the first intermediate product resin a second mixture comprised of at least one polymerizable monomer compound, wherein the polymerizable monomer compound of the second mixture is different from the polymerizable monomer compound of the first mixture, to form a combined mixture; heating the combined mixture to form a third mixture comprised of a block copolymer thermoplastic resin comprised

of a first product resin formed from the first intermediate product resin and added the second monomer; cooling the third mixture; and sequentially repeating the preceding steps of adding, heating and cooling, N times, to form a fourth mixture containing a multiblock copolymer thermoplastic resin having N+2 blocks and wherein N is a number representing the number of times the adding and heating sequence is repeated, and wherein the multiblock copolymer thermoplastic resin possesses a narrow polydispersity and a modality of 1. Added monomers can be water soluble, water insoluble, intermediate solubility, or soluble in both water and organic solvents. Judicious selection of the water solubility properties of added monomers and the resulting polymeric segment(s) enables convenient synthetic routes to block and multiblock copolymers with narrow polydispersities that are useful, for example, as surfactants and emulsifiers.

In yet other embodiments of the present invention, there are provided processes for polymerizing monomers comprising: (a) forming a reaction mixture by feeding into a reactor containing water or aqueous solutions with water miscible cosolvents; (i) one or more monomer solutions or suspensions thereof; (ii) a sterically hindered phenoxy stable free radical compound derived from the corresponding phenol or any of the aforementioned suitable stable free radical compounds and derivatives thereof, or a solution thereof; and (iii) a free radical initiator, or a solution thereof, in an effective amount for initiating polymerization of the monomers; and (b) heating the reaction mixture from about 100°C to about 250°C to form a homopolymer or copolymeric resin with a narrow polydispersity and high with conversion. This process embodiment can be accomplished by adding one or more monomers, a free radical initiator, and a suitable stable free radical, such as a phenoxy radical, simultaneously or sequentially in the order (i), (ii), and then (iii).

One class of monomers suitable for use in the present invention are carboxylic acid or acrylic monomers, that is C₃-C₆ monoethylenically unsaturated monocarboxylic acids, and the alkali metal and ammonium salts thereof. The C₃-C₆ monoethylenically unsaturated monocarboxylic acids include acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid, and acryloxypropionic acid.

Other suitable monomers are carboxylic acids, such as C₄-C₆ monoethylenically unsaturated dicarboxylic acids and the alkali metal and ammonium salts thereof, and the anhydrides of the cis dicarboxylic acids. Suitable examples include maleic acid, maleic anhydride, itaconic acid, mesaconic acid, fumaric acid, and citraconic acid.

Acid containing monomers useful in this invention may be in their acid forms or in the form of the alkali metal or ammonium salts of the acid. Suitable bases useful for neutralizing the monomer acids include sodium hydroxide, ammonium hydroxide, potassium hydroxide, and the like. The acid monomers may be neutralized to a level of from 0 to 50 percent and preferably from 0 to about 20 percent. More preferably, the carboxylic acid monomers are used in the completely neutralized form. Partial neutralization of the carboxylic acid monomers minimizes or eliminates corrosion on parts of the reaction equipment, but conversion of the monomers into polymer product may be diminished, for the aforementioned reasons. The acidic or labile proton containing monomers may be neutralized prior to, during, or after polymerization. The polymer products are often particularly useful in their partially or completely neutralized form.

In addition, the free radical reactive monomers that are useful in the present invention may be monoethylenically unsaturated carboxylic acid-free monomers. Suitable monoethylenically unsaturated carboxylic acid-free monomers can also be copolymerizable with the carboxylic containing monomers, for example, alkyl esters of acrylic or methacrylic acids; hydroxyalkyl esters of acrylic or methacrylic acids; acrylamides, vinylpyrrolidone; styrene; hydroxylated styrenes; styrenesulfonic acid and salts thereof; vinylsulfonic acid and salts thereof; and 2-acrylamido-2-methylpropane-sulfonic acid and salts thereof.

Monomers, polymers and copolymers containing the above mentioned acidic functionality can, in embodiments, be separated from one another or from the polymerization reaction mixture by, for example, changing the pH of the reaction media and other well known conventional separation techniques.

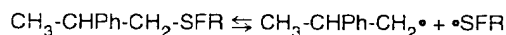
Suitable initiators for the processes of the present invention are any conventional free radical initiators which have a half-life of at least 1 second at the polymerization temperature. Preferably, the initiator will have a half life of from about 10 second to about 2 hours, more preferably from about 10 seconds to about 10 minutes at the polymerization reaction temperature. These initiators include, but are not limited to oxygen, hydrogen peroxide, certain alkyl hydroperoxides, dialkyl peroxides, peresters, percarbonates, peroxides, persulfates and azo initiators. The initiators are normally used in amounts of from about 0.05 percent to about 33 percent based on the weight of total polymerizable monomer. A preferred range is from about 0.5 to about 20 percent by weight of the total polymerizable monomer. In embodiments, the molar ratio of monomer to stable free radical agent to free radical initiator compounds is from about 50:0.2:1.0 to about 20,000:2.5:1.0. Preferred free radical initiators do not react with or degrade the stable free radical compounds with the exception of the aforementioned in situ stable free radical generation resulting from the reaction of the stable free radical precursor compound with a free radical fragments species. Redox initiators may also be selected. Redox initiators may be used in amounts of 0.05 percent to 16 percent, based on the weight of total monomer and preferably, from about 0.5 to about 5 percent by weight of total monomer. It is preferred that the level of these initiators, if used, be minimized.

The stable free radical compound or agent selected for use in the present invention may be any known non-nitroxyl type stable free radical agent which enables the objects and improvements of the present invention to be achieved.

Surprisingly and unexpectedly, the nitroxyl stable free radical compounds, and related derivatives, while quite satisfactory for the purpose of moderating the polymerization of a wide variety of different monomer and comonomer types, these compounds were found to be less effective at either higher temperatures or in the presence of acidic promoter compounds. The reduced effectiveness of the nitroxyl type stable free radical compounds at elevated temperatures or in the presence of acidic promoter compounds is believed to be attributable to known thermal and acidic instability, respectively, of these compounds. The instability of nitroxyl stable free radical compounds is documented in, for example, L.B. Volodarsky, V.A. Reznikov, and V.I. Ovcharenko, *Synthetic Chemistry of Stable Nitroxides*, CRC Press, Boca Raton, Florida, 1993 and also L. Berliner, *Spin Labeling Theory and Applications*, Academic Press, New York, 1976. The acidic instability of the nitroxide is believed to lead to, for example, conversion of the nitroxyl free radical functionality (= N-O•) to the corresponding ineffective hydroxyl amine compound (= N-OH).

A solution to the aforementioned problem of nitroxyl stable free radical compound thermal and acidic instability was achieved in the present invention by employing, for example, non-nitroxyl stable free radical compounds in the aforementioned elevated temperature or acidic, stable free radical polymerization process conditions.

The stability of the polymer-SFR bond can be estimated by calculation of bond dissociation enthalpies for the reaction



using semi-empirical molecular orbital calculations.

Table 1:

Calculated Bond Strength with an Analog of a Growing Polystyrene Chain Radical		
Stable Free Radical	Bond Strength (kcal/mole)	Comments
Benzoyloxy $\text{PhCO}_2\cdot$	80	Bond too strong; acts an initiator species
iniferter $[(\text{CH}_3)_2\text{N}](\text{C}=\text{S})\text{S}\cdot$	38	Bond is strong; slow polymerization Not sufficiently hindered; acts an initiator
cyclic 6-membered nitroxide: TEMPO	26	Weak bond; hindered; slow rate below about 125°C
cyclic 5-membered nitroxide: PROXYL	10	Very weak bond; more hindered and fast rate at about 100°C

Table 1 shows that the TEMPO nitroxyl free radical compound does form a stable but relatively weak bond with an analog of a growing polystyrene chain, of about 26 kcal/mole that is thermally labile. Based on these calculations, it can be shown that TEMPO controls free radical polymerizations, generating polymers with narrow molecular weight distributions, but slowly below 125°C. These calculations also predicted that PROXYL nitroxide SFR forms an even less stable bond of 10 kcal/mole. It was shown experimentally that PROXYL free radical provides for a faster rate of monomer polymerization compared to the TEMPO free radical. The C-O bond of a nitroxide-polymer adduct, of about 10 to about 26 kcal/mole, is much weaker bond than that for the corresponding C-S thiocarbamate iniferter-polymer adducts disclosed in the literature, at about 37 to 44 kcal/mole, reference, for example, T. Otsu and M. Yoshida, *Makromol Chem., Rapid Comm.*, 3, 127-132 (1982). The bond between the iniferter and the growing chain radical is too strong, so that polymerization rate is too slow to be useful. Similarly, benzoyloxy radicals, with a bond strength of about 80 kcal/mole, form a bond which is too stable to be thermally labile to be useful as a stable free radical agent in narrow polydispersity polymerization processes under the heating conditions of from about 100 to 250°C. Thus, as supported by the accompanying calculated bond strength energies in Table 1, bond strength values appear to be a good measure for evaluating various free radical species as potential stable free radical agent compounds for controlling molecular weight and polydispersity in stable free radical moderated polymerization processes while affording reasonable, that is, industrially acceptable, polymerization rates.

Other problems associated with selecting stable free radical compounds for use in stable free radical mediated narrow polydispersity polymerization processes include the degree of molecular structure steric hindrance in the immediate vicinity of the stable free radical bearing atom. Iniferter compounds are not sterically hindered to any extent, and thus these compounds are themselves capable of initiating new polymerization species throughout a polymerization process, thereby leading to broadening of the molecular weight distributions. Thus, it is not surprising that it has not been possible until recently to produce narrow polydispersity resins using iniferters, reference for example, Otsu

et. al., *Macromolecules*, 25,5554-5556 (1992). Also, it should be evident from the above considerations that peroxides, such as benzoyl peroxide, are very good initiators, and thus will fail to give narrow polydispersity resins if peroxides were to be used in the role of a stable free radical compound, that is, peroxides readily initiate polymerization; the peroxide-polymer bond is relatively strong, relatively thermally robust, and essentially irreversible for the temperature range 100 to 250°C; and the benzoyl radical species is relatively sterically unhindered.

Nitroxides are not known to be free radical initiators; on the contrary these compounds are known to be free radical scavengers or free radical inhibitors at lower temperatures, such as below 100°C. However, cyclic nitroxyl or nitroxide free radical compounds have other shortcomings, for example, TEMPO is plagued by competing side reactions such as ring opening, reductive elimination reactions, and the like reactions early on in polymerization processes additionally employing monomer and a free radical initiator such as benzoyl peroxide. The PROXYL compound has fewer side reactions than the TEMPO, but PROXYL is considerably more expensive than the TEMPO compound. In addition, many nitroxide compounds react with free radical initiators, such as bis azo compounds and benzoyl peroxide, in the absence of reactive monomer, and which undesirable side reaction unnecessarily consumes expensive nitroxide compounds and produces wasteful non polymeric byproducts. Calculations in Table 2 show bond enthalpies between an analog or model

Table 2:

Calculated Bond Strengths of Stable Free Radical Compounds of an Analog of a Growing Polystyrene Chain	
Stable Free Radical	Bond Strength (kcal/mole)
trinitrophenyl-N',N'-diphenylhydrazine	61.4
phenoxy Ph-O•	45.5
benzoxolane radical (R,R ₁ , and R ₂ = CH ₃)	37.8
α-tocopherol radical derivative (PMC)	37.4
di- <i>t</i> -butylphenoxy where	
X = H	37.4
<i>p</i> -OCH ₃	35.8
<i>p</i> -NO ₂ ; and	41.6
<i>p</i> -CH ₃	37.7
dithiocarbamate initiators	38-45
nitroxides	10.26

compound of a growing polystyrene chain and stable free radical derivative compounds based on phenoxys, tocopherols, and benzoxolanes. The adduct bonds formed by these stable free radical derivatives are of lower energy or less stable than, for example, dithiocarbamate iniferters, but they are more stable than nitroxides. Therefore, these bonds are expected to break more readily than the corresponding iniferter adducts, but not as readily as the corresponding nitroxide adducts. The aforementioned bond strengths should be considered as calculated maximum values, as they can be lowered by, for example, the addition or inclusion of electron donating groups. As shown for di-*t*-butyl substituted phenoxy radical, the addition of a para substituent influences the polymer SFR bond strength. The sterically hindered phenoxy radicals are not likely to initiate polymerization as they are too hindered and are well known as inhibitors and radical scavengers, similar to the nitroxide stable free radical compounds. Adding sterically hindering groups around or about the radical bearing atom reduces the likelihood that these compounds would induce free radical initiation of polymerization, and further reduces the possibility of side reactions on the aromatic nucleus at these sites and reduces the bond strength between the stable free radical agent and the polymer chain. Thus, free radical compounds that satisfy the above mentioned requirements, such as bond strength and steric hindrance about the free radical center are considered preferred alternatives to nitroxide stable free radical compounds to achieve narrow polydispersity resins in stable free radical mediated processes. Many of these alternative materials are relatively inexpensive and are readily commercially available compared to nitroxide compounds. Commercially available precursor materials, from for example, Aldrich Chemical in amounts less than about 1kg include: 2,6-di-*t*-butyl-4-methylphenol (\$27/kg); 2,4,6-tri-*t*-butylphenol (\$89/kg); 2,6-di-*t*-butyl-4-methoxyphenol, α-tocopherol or Vitamin E (\$200/kg); and 2,2,5,7,8-pentamethyl-6-chroman-ol or PMC. In contrast, TEMPO, the least expensive nitroxide available from Aldrich, is about \$4,000 per kilogram. The free radical center or species can be introduced into the aforementioned alternative stable free radical precursor materials by reaction with initiators such as benzoyl peroxide and the like reactants. Triphenyl hydrazine compounds, such as trinitrophenyl-N',N'-diphenylhydrazine (DPPH), are also believed to be useful as

stable free radical compounds for the polymerization processes of the present invention and for those derivatives with suitably strong electron donating groups which provide a sufficiently low bond strength between the DPPH and the polymer species.

Although not desired to be limited by theory, the calculations also suggest that with all other factors being equal, the lower the bond dissociation energy the more labile the polymer-SFR or C-O bond is and the reaction should proceed at a faster rate at a given temperature. In addition, the calculations also correctly predict that stable free radicals have an endothermic enthalpy of reaction with styrene monomer and thus are incapable of initiating new polymer chains which enthalpy condition is believed to be a requirement for a living polymerization system to give narrow molecular weight distributions.

The monomers of the present invention can be polymerized in a variety of polymerization reaction media. The reaction mixture may contain from about 95 to about 98 percent by weight, preferably from about 5 to about 90 percent by weight monomer with the balance comprised of other reactants, reagents, comonomers, and optional solvents, diluents, or additives.

The improved polymerization reactions of the present invention can be supplemented with a solvent or cosolvent if desired to help ensure that the reaction mixture or at least the monomer containing portion remains a homogeneous single phase throughout the monomer conversion. Any solvent or cosolvent may be selected so long as the solvent media is effective in providing a solvent system which avoids precipitation or phase separation of the reactants or polymer products until after all the solution polymerization reactions have been completed. Exemplary solvent or cosolvents are polymer product compatible aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkyl pyrrolidinones, N-alkyl pyrrolidones, polyethylene glycols, polypropylene glycols, amides, carboxylic acids and salts thereof, esters, organosulfides, sulfoxides, sulfones, alcohol derivatives, hydroxyether derivatives such as butyl CARBITOL® or CELLOSOLVE®, amino alcohols, ketones, and the like, derivatives thereof, and mixtures thereof. When mixtures of water and water soluble or miscible organic liquids are selected as the reaction media, the water to cosolvent weight ratio typically ranges from about 100:0 to about 10:90, and preferably from about 97:3 to about 25:75.

Temperature of the polymerization may range from about 100°C to about 250°C, preferably from about 110°C to about 180°C. At temperatures below about 60 to 80°C, the reaction rate is slow and industrially impractical without the aid of an acid or base accelerating additive compound. At temperatures above about 250°C, conversion of the monomer into polymer decreases, and uncertain and undesirable by-products are formed. Frequently, these by-products discolor the polymer mixture and may necessitate a purification step to remove them or they may be intractable.

Since solvent and cosolvent admixtures can be used as the reaction media, the elevated temperatures of the polymerization require that the polymerization reactor be equipped to operate at elevated pressure.

The molecular weights referred to are measured by gel permeation chromatography using, for example, a polyethylene oxide standards for water soluble polymers and polystyrene standards for organic soluble polymers unless specifically stated otherwise.

The present invention provides several specific advantages in embodiments as follows.

With the process of the present invention, polymer product polydispersities can be varied from between approximately 1.0 to approximately 2.0, or lower or higher if desired depending on the monomer/comonomer system by varying the ratio of stable free radical agent to free radical initiator molar concentration. When the polymerization process conditions of the present invention are attempted with bulky or sterically hindered, for example, alkyl acrylate type monomers without using the a stable free radical (SFR) agent additive, considerably broader molecular weight resins are obtained and autopolymerization effects are observed, or alternatively, no product polymer is formed.

During the reaction of monomer or mixtures of monomers to form polymers, the reaction time may be varied over about 30 minutes to 60 hours, preferably between about 2 to 10 hours and optimally about 3 to 7 hours. The optimal reaction time may vary depending upon the temperature, the volume and scale of the reaction, and the quantity and type of polymerization initiator and stable free radical agent selected.

Preferred initiator compounds are: t-butyl peroxy isobutyrate (120°C); t-butyl peroxy 2-ethylhexanoate (95°C); t-butyl pivalate (76°C); and t-amyl peroxy 2-ethyl hexanoate (92°C). Particularly preferred free radical initiators are azobisalkylnitrile and diaroxy peroxide compounds.

The monomer or monomers to be polymerized in embodiments can be dissolved in water or aqueous mixtures of polar protic or aprotic organic solvents. The resultant aqueous solution usually contains a suitable water-soluble, free-radical generating initiator such as a peroxide or a persulfate, and the like, as defined above. The monomer or monomers are used in effective amounts relative to the free radical initiator, and stable free radical agent, as defined hereinafter.

The stable free radical agent used for controlling polymerization processes of monomers or comonomers of the present invention can be any stable free radical compound which fulfills the above-mentioned criteria. These stable free radical agent materials are well known in the literature as free radical polymerization inhibitors or free radical scavengers, for example, the aforementioned sterically hindered and highly "stable" stable free radical compounds, reference Macromolecules, Vols I and II, H.G. Elias Ed., Plenum Publishers, Second Edition, New York, 1984. However,

under the polymerization conditions of the present invention, the stable free radical agents function not as inhibitors but as moderators to harness the normally highly reactive and indiscriminate propagating intermediate free radical polymer chain species. Other suitable stable free radicals that may be used in conjunction with polymerizing monomers or comonomers in the polymerization processes of the present invention are disclosed in U.S. Patent Nos. 3,600,169 and 5,324,604, the disclosures of which are incorporated by reference herein in their entirety. The stable free radical agents are preferably soluble in the monomer phase, where predominantly all the polymerization of monomers occurs. Stable free radical agents which have limited monomer solubility are still useful, but may require a monomer miscible cosolvent or else these stable free radical compounds tend to result in less predictable polymerization processes. If the stable free radical agent separates out of the monomer phase to any great extent then the balance desired between the mole ratio of the stable free radical agent, free radical initiator, and propagating free radical polymer chain species may be upset.

The molar ratio of the stable free radical (SFR) agent to free radical initiator (INIT) residing in the monomer phase is from about 0.5 to 5.0, and preferably in the range from about 0.4 to 4.0. Although not wanting to be limited by theory, in an embodiment, the molar ratio [SFR:INIT] of stable free radical agent, for example, 2,4,6-tri-tert-butyl phenoxy radical, to free radical initiator, for example, benzoyl peroxide is about 2.0 and is believed to be important for success of the process. If the [SFR:INIT] is too high then the reaction rate is noticeably inhibited. If the [SFR:INIT] is too low then the reaction product has undesired increased polydispersity. It should be noted that when alkyl acrylic acid or alkyl acrylate ester compounds are polymerized to polyalkylacrylate derivatives at comparatively high temperatures without the stable free radical agent of the present process, the product polymers isolated have polydispersities in excess of 2.0 and above.

In embodiments, the molar ratio of monomer content to stable free radical agent to free radical initiator is from about 6,000:2.5:1 to about 10,000:2.5:1 and preferably in the range of about 125:2.0:1 to about 7,000:1.3:1.

Processes of the present invention, in embodiments, provide for selective low, intermediate, and high monomer to polymer conversion rates, or degrees of polymerization, and preferably, for example, of 90 percent by weight or greater.

The low weight average molecular weight resin products having narrow polydispersity properties, as is also the situation with intermediate and high molecular weight products of the present invention, may be obtained without the use of a chain transfer agent.

Processes of the present invention, in embodiments also provide for relatively high weight average molecular weights, from weight average molecular weights ranging in size of from about 2,000 to about 200,000 while delivering narrow polydispersity products.

The polymerization reaction rate of the monomers may, in embodiments, be inhibited or accelerated and the reaction time influenced by the addition of a minor amount of a protic acid such as sulfuric, hydrochloric, and the like, and organic sulfonic and carboxylic acids. The added acid may have a profound or very little effect on the polymerization rate, depending upon a variety of reaction variables and conditions. Excessive addition of inorganic and organic acid beyond equimolar amounts compared to the stable free radical agent causes the resin polydispersity to broaden. In embodiments, the protic acid source may be an acid functional group contained in either the stable free radical agent or in the free radical initiator compound.

The polymeric products of the present invention may be optionally crosslinked with, for example, known crosslinking, coupling, or curing agents such as divinyl benzene and the like, either *in situ* or in a separate post polymerization process step.

Additional optional known additives may be used in the polymerization reactions which do not interfere with the objects of the invention and which may provide additional performance enhancements to the resulting product, for example, colorants, lubricants, release or transfer agents, surfactants, stabilizers, antifoams, antioxidants, and the like.

Polymer resins possessing a discrete mixture of monomodal, that is a well defined multimodal molecular weight distribution may in embodiments thereof provide several advantages, particularly for electrophotographic toner compositions such as: melt rheology properties including improved flow and elasticity; and improved performance properties such as triboelectrification, admix rates, and shelf life stabilities. weight indicates that a nearly linear relationship holds for bulk polymerization reaction media using stable free radical agent moderated processes and which relationship is believed to be operative in the present invention.

Toner compositions can be prepared by a number of known methods, such as admixing and heating resin particles obtained with the processes of the present invention such as styrene butadiene copolymer derivatives, pigment particles such as magnetite, carbon black, or mixtures thereof, and cyan, yellow, magenta, green, brown, red, or mixtures thereof, and preferably from about 0.5 percent to about 5 percent of charge enhancing additives in a toner extrusion device, such as the ZSKS3 available from Werner Pfleiderer, and removing the formed toner composition from the device. Subsequent to cooling, the toner composition is subjected to grinding utilizing, for example, a Sturtevant micronizer for the purpose of achieving toner particles with a volume median diameter of less than about 25 microns, and preferably of from about 6 to about 12 microns, which diameters are determined by a Coulter Counter. Subse-

quently, the toner compositions can be classified utilizing, for example, a Donaldson Model B classifier for the purpose of removing toner fines, that is toner particles less than about 4 microns volume median diameter.

Illustrative examples of suitable toner resins selected for the toner and developer compositions of the present invention include styrene acrylates, styrene methacrylates, styrene butadienes, vinyl resins, including homopolymers and copolymers of two or more vinyl monomers. Other preferred toner resins include styrene/n-butyl acrylate copolymers, PLIOLITES®; suspension polymerized styrene butadienes, reference U.S. Patent 4,558,108.

In toner compositions, the resin particles are present in a sufficient but effective amount, for example from about 70 to about 90 weight percent. Thus, when 1 percent by weight of the charge enhancing additive is present, and 10 percent by weight of pigment or colorant, such as carbon black, is contained therein, about 89 percent by weight of resin is selected. Also, the charge enhancing additive may be coated on the pigment particle. When used as a coating, the charge enhancing additive is present in an amount of from about 0.1 weight percent to about 5 weight percent, and preferably from about 0.3 weight percent to about 1 weight percent.

For the formulation of developer compositions, there are mixed with the toner particles carrier components, particularly those that are capable of triboelectrically assuming an opposite polarity to that of the toner composition. Accordingly, the carrier particles are selected to be of a negative polarity enabling the toner particles, which are positively charged, to adhere to and surround the carrier particles. Illustrative examples of carrier particles include iron powder, steel, nickel, iron, ferrites, including copper zinc ferrites, and the like. Additionally, there can be selected as carrier particles nickel berry carriers as illustrated in US-A-3,847,604e. The selected carrier particles can be used with or without a coating, the coating generally containing terpolymers of styrene, methylmethacrylate, and a silane, such as triethoxy silane, reference US-A-3,526,533, US-A-4,937,166, and US-A-4,935,326, including for example KYNAR® and polymethylmethacrylate mixtures (40/60). Coating weights can vary as indicated herein; generally, however, from about 0.3 to about 2, and preferably from about 0.5 to about 1.5 weight percent coating weight is selected.

Furthermore, the diameter of the carrier particles, preferably spherical in shape, is generally from about 50 microns to about 1,000 microns, and in embodiments about 175 microns thereby permitting them to possess sufficient density and inertia to avoid adherence to the electrostatic images during the development process. The carrier component can be mixed with the toner composition in various suitable combinations, however, best results are obtained when about 1 to 5 parts per toner to about 10 parts to about 200 parts by weight of carrier are selected.

The toner and developer compositions may be selected for use in electrostatographic imaging apparatuses containing therein conventional photoreceptors providing that they are capable of being charged positively or negatively. Thus, the toner and developer compositions can be used with layered photoreceptors that are capable of being charged negatively, such as those described in U.S. Patent 4,265,990.

The toner compositions prepared from resins of the present invention possess desirable narrow charge distributions, optimal charging triboelectric values, preferably of from 10 to about 40, and more preferably from about 10 to about 35 microcoulombs per gram as determined by the known Faraday Cage methods with from about 0.1 to about 5 weight percent in one embodiment of the charge enhancing additive; and rapid admix charging times as determined in the charge spectrograph of less than 15 seconds, and more preferably in some embodiments from about 1 to about 14 seconds.

The following Examples are being supplied to further define various species of the present invention, it being noted that these Examples are intended to illustrate and not limit the scope of the present invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Phenoxy Stable Free Radical Moderated Polymerization of n-Butyl Acrylate

n-Butyl acrylate monomer (5 mL), AIBN free radical initiator (100 mg) and 2,4,6-tri-tert-butyl phenoxy stable free radical (84 mg) are mixed together and heated in an oil bath maintained at a temperature of 165°C, under argon, for 3.5 hours. Samples (100 microliter aliquots) are removed at the time intervals and indicate that the molecular weights increase with time with no significant broadening of the polydispersity (PD).

EXAMPLE II

When Example I is repeated, with the exception that less AIBN free radical initiator is used, a higher molecular weight homopolymer of poly(n-butyl acrylate) resin can be obtained. Thus, when n-butyl acrylate (5 mL), AIBN (50 mg) and 2,4,6-tri-tert-butyl phenoxy stable free radical (84 mg) are mixed together and heated in an oil bath, under argon, for about 4 hours, a resin with approximately $M_n = 2,486$, $M_w = 3,641$, and $PD = 1.46$ is obtained.

EXAMPLE III

When Example II is repeated, with the exception that about three times as much monomer is used, an even higher molecular weight poly(n-butyl acrylate) resin is obtained. Thus, when n-butyl acrylate (15mL), AIBN (50 mg) and 2,4,6-tri-tert-butyl phenoxy stable free radical (84 mg) are mixed together and heated in an oil bath, under argon, for about 9 hours, a resin with approximately $M_n=9,198$, $M_w=15,878$ and $PD=1.73$ is obtained. Washing with methanol removes some oligomers to yield a thick oil with $M_n = 16,736$, $M_w = 20,577$, and $PD = 1.23$.

EXAMPLE IV

When the polymerization is repeated with DMSO, as a polymerization solvent, a narrower polydispersity can be obtained. Thus, when n-butyl acrylate (10 mL), AIBN (50 mg) and 2,4,6-tri-tert-butyl phenoxy stable free radical (115 mg) in 20 mL of DMSO are mixed together and heated in an oil bath, under argon, for about 8 hours, a resin with $M_n = 6,577$, $M_w = 8,923$ and $PD = 1.36$ is obtained. The same experiment conducted without DMSO present gives a polymer product with $M_n = 4,030$, $M_w = 6,953$, and $PD = 1.72$.

EXAMPLE V**Galvinoxyl Stable Free Radical Modulated Polymerization of n-Butyl Acrylate**

n-Butyl acrylate (3mL), AIBN free radical initiator (0.033 gm, 0.2 mmol) and galvinoxyl stable free radical (0.180 gm, 0.43 mmol, available from Aldrich Chemical Co.) were mixed together and heated in an oil bath, at about 145°C, under an argon atmosphere. The initial reaction mixture was a deep purple black color which gradually changed to a reddish brown as the reaction progressed. Samples (100 microliter aliquots) were removed from the mixture and analyzed by GPC after 5 minutes and 65 minutes, respectively. The results shown in the accompanying table indicate an increase in both M_w and M_n and most notably a decrease in the polydispersity (PD).

EXAMPLE VI

Example V was repeated with the exception that different amounts of galvinoxyl stable free radical were used at a lower temperature. Thus, when n-butyl acrylate (4mL), AIBN (0.033g, 0.2 mmol), and galvinoxyl in Reaction A using 0.129 gm, 0.3 mmol, or in Reaction B using 0.169 gm, 0.4 mmol, were heated in an oil bath at 125°C, Reaction A changed color after 3 minutes from

Sample	Time (min)	M_w	M_n	PD
1	5	4,476	1,373	3.26
2	65	4,605	1,927	2.39

very dark purple black to reddish brown, while Reaction B remained relatively dark throughout. Samples were removed and analyzed as indicated in the accompanying table with

Sample	Time (hr)	Reaction A (M_w)	Reaction B (M_w)
1	1.25	366	191
2	2.25	408	191
3	5.25	618	191
4	7.25	827	191

results indicating that the peak molecular weights of reaction A increased with increasing time, while for Reaction B the peak molecular weight remained essentially constant. Thus, the ratio of the stable free radical (SFR) to the free radical initiator (I) appears too important to the relative rate of increase in the molecular weight of the polymer products.

EXAMPLE VII

When Example IV Reaction B was repeated, that is with galvinoxyl (0.169 gm, 0.4 mmol), the GPC results shown

in the Table were obtained for the poly(n-butyl acrylate) polymer formed.

Sample	Time (min)	\overline{M}_w	\overline{M}_n	PD
1	5	257	106	2.42
2	17	1,106	699	1.58

EXAMPLE VIII

Magnetic Toner Preparation and Evaluation The polymer resin (74 weight percent of the total mixture) obtained by the stable free radical polymerization processes in Example I may be melt extruded with 10 weight percent of REGAL 330® carbon black and 16 weight percent of MAPICO BLACK® magnetite at 120°C, and the extrudate pulverized in a Waring blender and jetted to 8 micron number average sized particles. A positively charging magnetic toner may be prepared by surface treating the jetted toner (2 grams) with 0.12 gram of a 1:1 weight ratio of AEROSIL R972® (Degussa) and TP-302 a naphthalene sulfonate and quaternary ammonium salt (Nachem/Hodogaya S1) charge control agent.

Developer compositions may then be prepared by admixing 3.34 parts by weight of the aforementioned toner composition with 96.66 parts by weight of a carrier comprised of a steel core with a polymer mixture thereover containing 70 percent by weight of KYNAR®, a polyvinylidene fluoride, and 30 percent by weight of polymethyl methacrylate; the coating weight being about 0.9 percent. Cascade development may be used to develop a Xerox Model D photoreceptor using a "negative" target. The light exposure may be set between 5 and 10 seconds and a negative bias used to dark transfer the positive toned images from the photoreceptor to paper.

Claims

1. A polymerization process comprising:

heating a mixture comprised of a free radical initiator, a stable free radical agent comprised of a compound with a sterically hindered atom bearing a stable free radical, selected from the group consisting of sterically hindered organic hydrazyls, organic verdazyls, pyridinyl compounds, organic aroxyls, aryl alkyls and aryl cycloalkyls in which the unpaired electron is on a carbon atom in the alkyl or cycloalkyl group, and compatible mixtures thereof, at least one free radical reactive polymerizable monomer compound, and optionally a solvent, to form a polymer with a high monomer to polymer conversion and a narrow polydispersity, wherein said polymer is comprised of a covalently bound free radical initiator fragment at one end and a covalently bound stable free radical compound at the other end of the polymer, and wherein said stable free radical agent has high thermal, acidic, and photochemical stability.

2. A process in accordance with claim 1, wherein the free radical initiator is selected from the group consisting of organic peroxides, organic persulfates, inorganic persulfates, peroxydisulfate, azobisalkylnitriles, peroxy-carbonates, perborates, percarbonates, perchlorates, peracids, hydrogen peroxides, and mixtures thereof.

3. A process in accordance with claim 1 or claim 2, wherein the polymerizable monomer is a free radical reactive unsaturated compound selected from the group consisting of styrene and derivatives thereof, conjugated dienes and derivatives thereof, acrylates and derivatives thereof, 9-vinyl acetate and derivatives thereof, amine, carboxyl, aldehyde, alkyl, cyano, and hydroxyl substituted acrylic acids and acrylic acid esters having from 2 to about 20 carbon atoms; acrylamide; methacrylamide; acrylic acid; methacrylic acid; acrolein; dimethylaminoacrylate; hydroxy-lower alkyl, and amino-lower alkyl acrylates of the formula $\text{CH}_2 = \text{C}(-\text{R}^1)-(\text{C}=\text{Z})-\text{R}^2$ where R^1 is hydrogen, R^2 is selected from the group consisting of $-\text{OR}^1$ and $-\text{NR}^1_2$, and wherein Z is selected from the group consisting of oxygen and sulfur atoms.

4. A process according according to any one of claims 1 to 3, further comprising cooling the heated mixture to below 40°C to temporarily suspend the polymerization process or upon completion of the polymerization reaction, and, optionally, wherein the polymer produced therein is washed and dried upon isolation.

5. A process in accordance with claim 1 wherein the stable free radical agent to free radical initiator molar ratio is from about 0.4 to 2.5; or from about 0.9 to 2.0; and/or wherein the monomer to free radical initiator molar ratio is from about 100:1 to about 20,000:1.

6. A free radical polymerization process for the preparation of thermoplastic resins or elastomers comprising:

heating from about 80 to about 200°C for a period of about 30 minutes to about 10 hours a mixture comprised of a diaryloyl free radical initiator compound, a stable free radical agent derived from 2,4,6-tri-tert-butyl phenol, and at least one polymerizable monomer compound to form said thermoplastic resin or elastomer;

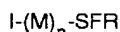
cooling said mixture;

optionally isolating said thermoplastic resin; and

optionally washing and drying said thermoplastic resin or elastomer, wherein said thermoplastic resin or elastomer possesses a narrow polydispersity of from about 1.1 to about 1.7, wherein said resin contains from about 5 to about 4,000 contiguously bonded monomer units, wherein an initiator fragment from said diaryloyl initiator compound is covalently bonded to one end and said stable free radical agent is covalently bonded to the other end of said resin or elastomer, and wherein a monomer to polymer conversion from about 10 to about 100 percent is achieved.

7. A polymer or copolymer resin composition obtained by the process of claim 1 wherein said resins or elastomers have a weight average molecular weight (M_w) of from about 2,000 to 200,000 and a number average molecular weight (M_n) of from about 1,000 to about 100,000 and a polydispersity of about 1.0 to 2.0.

8. A thermoplastic polymer resin or elastomer of the formula



wherein I is a covalently bonded free radical initiator fragment, $(M)_n$ is at least one contiguous polymeric segment comprised of at least one free radical polymerized monomer compound M, n is an integer from about 10 to about 20,000 and represents the total number monomer units contained in the polymeric segment, and SFR is a covalently bonded stable free radical agent, wherein the stable free radical agent possesses high thermal stability, high acid stability, high photochemical stability, low toxicity, and high reactivity and high dissociability with propagating free radical polymeric species and is comprised of a sterically hindered stable free radical bearing atom, and is selected from highly substituted members of the group consisting of organic hydrazyls, organic verdazyls, pyridinyl compounds, organic aroxyls, aryl alkyls and aryl cycloalkyls in which the unpaired electron is on a carbon atom in the alkyl or cycloalkyl group, and compatible mixtures thereof.

9. A polymer resin or elastomer in accordance with claim 44 wherein the stable free radical agent is thermally stable up to about 250 to about 300 °C; or wherein the stable free radical agent is stable in aqueous acidic media at a pH of about 1.0 and above; or wherein the stable free radical agent is photochemically stable when irradiated with wavelengths in the range from about 200 to about 800 nm; or wherein the stable free radical agent has a low toxicity as measured by LD₅₀ (rats) of greater than about 500 to about 1,000 mg/kg; or wherein the stable free radical agent is substantially free of highly corrosive attributes; or wherein the free radical agent of the stable free radical form is generated by oxidizing the corresponding protonated compound; or wherein the stable free radical agent 2,4,6-tri-tert-butylphenoxy radical is selected; or wherein the free radical form of the stable free radical agent has a half life of greater than about 10 hours at about 200°C in the absence of polymerization reaction components selected from the group of monomer, polymer, and free radical initiator.

10. A polymer resin or elastomer in accordance with claim 8 wherein the free radical initiator fragment (I) arises from thermal or photochemical decomposition of the corresponding free radical precursor compound (I-I) selected from the group consisting of organic peroxides, organic persulfates, inorganic persulfates, peroxydisulfate, azobisalkylnitriles, peroxy carbonates, perborates, percarbonates, perchlorates, peracids, hydrogen peroxides, and mixtures thereof.

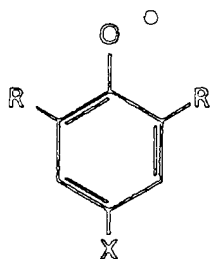


FIG. 1

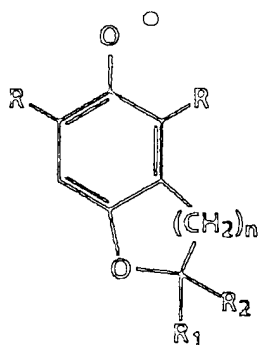


FIG. 2

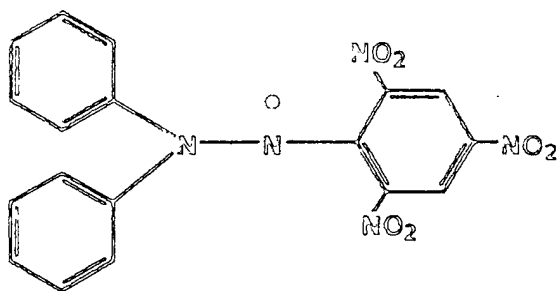


FIG. 3

